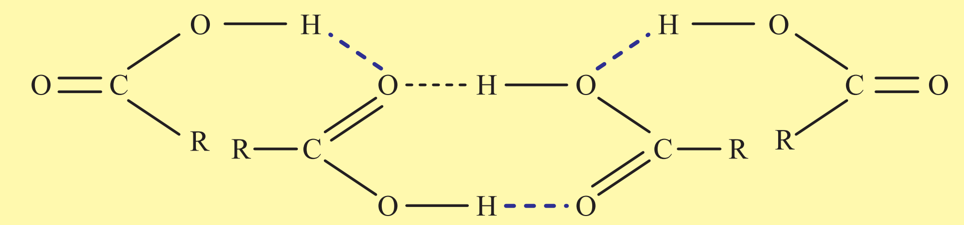
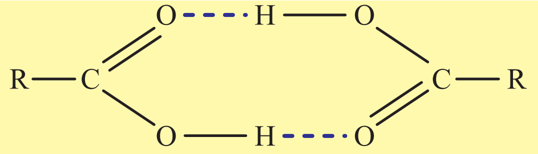
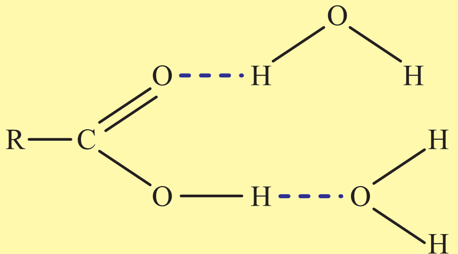
of comparable molecular mass. In liquid state, the carboxylic acid molecules are associated with other carboxylic acid by formation of strong hydrogen bonding. The hydrogen bonding is so strong that they are not broken even in vapour phase. **In vapour phase or in aprotic solvents most of the carboxylic acids exist as cyclic dimers.**



Association of carboxylic acid molecules in liquid state



Dimer form in aprotic solvent or vapour phase

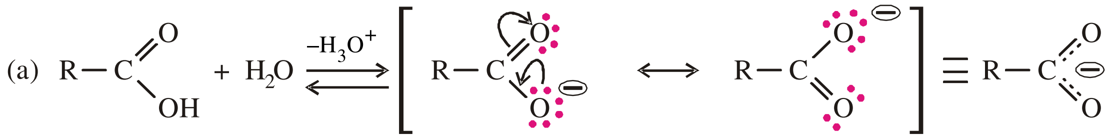


Hydrogen bonding in aqueous solution

Carboxylic acids in aqueous solution form intermolecular hydrogen bond with water molecules, so the carboxylic acids with lower molecular masses are soluble in water.

5.11 Chemical Reactions of Carboxylic Acids

Acidic nature of carboxylic acid : Alcohols, phenols and carboxylic acids contain an –OH group, but the carboxylic acids are much stronger acid than alcohols and phenols. Comparison of acidic character of alcohols, phenols and carboxylic acids are based on the stability of resonance structure of their negative ions.



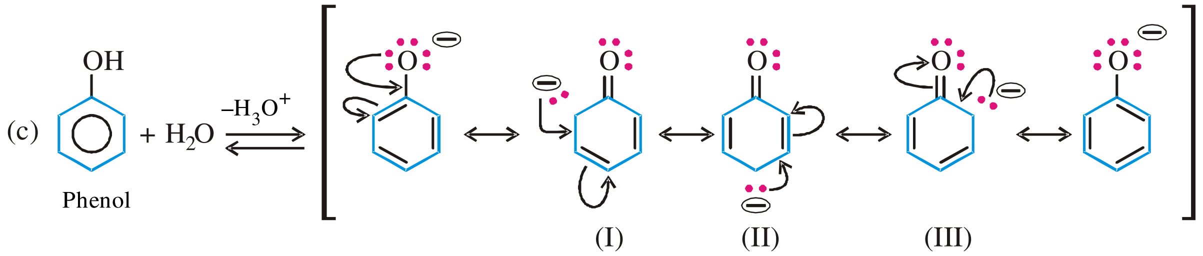
Carboxylic acid

Carboxylate ion stabilized by resonance.

(b) $R-OH + H_2O \rightleftharpoons RO^- + H_3O^+$

Alcohol

Not stabilized



As shown in reaction (a) carboxylate anions are stabilized by their resonance structures, so tendency to release proton is more, while the alkoxide ions as shown in reaction (b) are not stabilised by resonance, hence, alcohols have less tendency to release a proton, so the alcohols are much weaker acids than carboxylic acids, though both contain an –OH group. In case of phenoxide ion as shown in reaction (c) having resonating structure I to III, but the structures carry a negative charge on the less electronegative carbon atom. Therefore their contribution towards the resonance stabilization of phenoxide ion is very small, while in carboxylate ion the negative charge on the more electronegative oxygen atom, **so carboxylic acids are stronger acids than alcohols and phenols. but are weaker acids than the mineral acids** (HCl, HNO_3, H_2SO_4) and sulphonic acids. In aqueous solutions, the carboxylic acid ionizes and exist in dynamic equilibrium between carboxylate ion and hydronium ion.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

So the equilibrium constant can be expressed as $K_{eq} = \dfrac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$ (5.1)

Since water is taken in large excess hence $[H_2O]$ remains constant, so the equation (5.1) can be written as

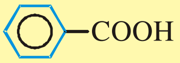
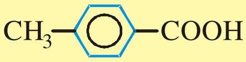
$$K_{eq} \times [H_2O] = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} = K_a \tag{5.2}$$

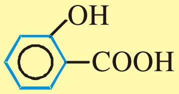
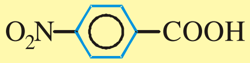
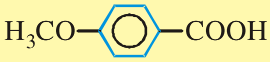
The equilibrium constant K_a is called the dissociation constant of the acid, and it varies with the temperature for a given acid. From equation (5.2) it is clear that at constant temperature, K_a is directly proportional to the $[H_3O^+]$. Therefore the value K_a is a measure of the acid strength of an acid, so higher the value of **K_a, greater is the tendency of the acid to ionize and hence stronger is the acid.** For convenience, the strength of an acid is generally indicated by its pK_a value, rather than its K_a value

$$pK_a = -\log K_a$$

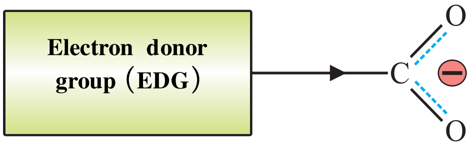
So, if carboxylic acid having smaller numerical value of pK_a, then it is very strong i.e. **better is a proton** donor. Strong acids have **pK_a values < 1,** the acids with pK_a values between **1 and 5** are considered to be moderately strong acids, weak acids have pK_a values between **5 and 15** and extremely weak acids have **pK_a values > 15.** K_a and pK_a values of some acids at 298 K temperature are given in table 5.6.

Table 5.6 K_a and pK_a values of some acids at 298 K (For information only)

Acid	K_a	pK_a	Acid	K_a	pK_a
HCOOH	17.7×10^{-5}	3.75	ICH_2COOH	67×10^{-5}	3.17
CH_3COOH	1.75×10^{-5}	4.76	$CH_2{=}CHCOOH$	5.5×10^{-5}	4.3
CH_3CH_2COOH	1.3×10^{-5}	4.88		6.3×10^{-5}	4.2
$ClCH_2COOH$	136×10^{-5}	2.87		4.2×10^{-5}	4.38

$Cl_2CHCOOH$	5530×10^{-5}	1.26		105×10^{-5}	2.98
Cl_3CCOOH	23200×10^{-5}	0.64		36×10^{-5}	3.44
FCH_2COOH	260×10^{-5}	2.59		3×10^{-5}	4.48
$BrCH_2COOH$	125×10^{-5}	2.90			

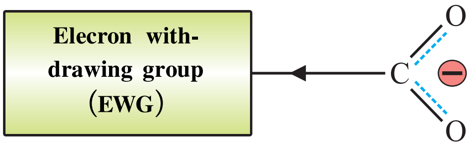
The acid strength of carboxylic acid depends on the effect of various substituents. For example,



(i) Effect of electron donating groups (EDG) :

The alkyl group has electron donating inductive effect (+I effect), hence it will increase the electron density in the –OH bond, so **release of** H^+ ions will be more difficult, hence, the formic acid is stronger acid than acetic acid. Further the +I effect of the alkyl groups increases in the order

$CH_3– < CH_3CH_2– < (CH_3)_2CH– < (CH_3)_3C–$ Hence the relative strength of carboxylic acid will be as **$CH_3COOH > CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C–COOH$**



(ii) Effect of electron withdrawing group (EWG) :

Electron withdrawing group having –I effect, and it decreases in the order –F > –Cl > –Br > –I > –Ph. So the strength of the carboxylic acids will be as.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > C_6H_5CH_2COOH$

Further, greater the number of electron withdrawing goups (substituents), stronger will be the acid (strength).

$Cl_3\ C\ COOH > Cl_2\ CH\ COOH > Cl\ CH_2\ COOH$

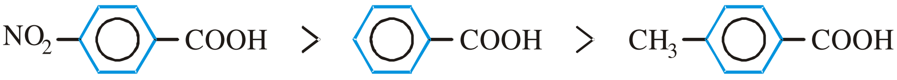
The inductive effect decreases rapidly with distance, so acidic strength order is

$$CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{C}HCOOH > CH_3\overset{\overset{\displaystyle Cl}{|}}{C}HCH_2COOH > \overset{\overset{\displaystyle Cl}{|}}{C}H_2CH_2CH_2COOH$$

(iii) The phenyl or vinyl group directly attached to carboxyl group have weaker electron donating effect than alkyl group. So unsubstituted aromatic carboxylic acids are stronger acids than unsubstituted aliphatic carboxylic acids, but formic acid does not contain any alkyl group, therefore it is stronger acid than unsubstituted aromatic acid, so the order of acidic strength is

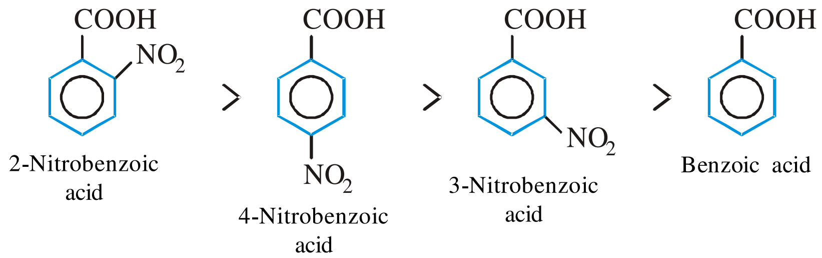
Formic acid > Benzoic acid > Acetic acid.

For substituted aromatic carboxylic acid the presence of electron withdrawing group on the phenyl or aromatic carboxylic acid increases their acidic strength, while electron donating group, decreases their acidic strength. For example,



4–Nitrobenzoic acid   Benzoic acid   4–Methylbenzoic acid.

Electron withdrawing or electron donating group effect is more pronounced at 1,2 position (ortho position) than 1,4 position (para position) than 1,3 position (meta position). For example the acid strength is



2-Nitrobenzoic acid

4-Nitrobenzoic acid

3-Nitrobenzoic acid

Benzoic acid

(1) Reactions involving cleavage of O–H bond : The reactions showing the acidic character of the carboxylic acids i.e. cleavage of O–H bond are given below :

(i) Reaction with metal : Carboxylic acids like alcohols react with electropositive metals such as Na, K, Ca, Mg, Zn etc. to form their respective salts and liberate H_2 gas. For example,

$$\underset{\text{Acetic acid}}{CH_3COOH} + Na \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \frac{1}{2} H_2$$

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Zn \rightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

(ii) Reaction with alkalies : Similar to phenols the carboxylic acids neutralize alkalies and form salts. For example,

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_4OH \rightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} + H_2O$$

(iii) Reaction with carbonates and hydrogen carbonates : However unlike phenols the carboxylic acids react with weaker bases such as carbonates and hydrogen carbonates to evolve CO_2 gas. For example,

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Na_2CO_3 \rightarrow \underset{\text{Sodium acetate}}{2CH_3COONa} + CO_2 + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaHCO_3 \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + CO_2 + H_2O$$

This reaction is used to detect the presence of –COOH group in organic compounds. As most of the phenols do not produce CO_2 gas with $NaHCO_3$. Hence this reaction is **also useful to distinguish phenols from carboxylic acids.**

(2) Reaction involving cleavage of C–OH bond : The hydroxyl group of a carboxylic acid like the hydroxyl group in alcohols, can be replaced (substituted) by group like –Cl, –OR', $–NH_2$ and –OCOR' to form acid chloride, esters, amides, and anhydrides, respectively. These derivatives are known as functional group derivatives of carboxylic acids.

(i) Formation of acid chlorides : Carboxylic acid reacts with $SOCl_2$ (thionyl chloride) or PCl_5 or PCl_3 to form acid chloride. For example,

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2(g) + HCl(g)$$

Acetic acid — Ethanoyl chloride (Acetyl chloride)

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

Acetic acid — Ethanoyl chloride (Acetyl chloride)

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

Acetic acid — Ethanoyl chloride (Acetyl chloride)

For the production of acid chloride, the reaction with $SOCl_2$ is preferred, because in this reaction the other two products SO_2 and HCl both are in gaseous state, so it is very easy to remove them from acid chloride, **hence purification of acid chloride becomes very easy.**

(ii) Formation of esters : When carboxylic acids are heated with alcohols or phenols in presence of con. H_2SO_4 or HCl, esters are formed. The reactions are known as esterifications **(Fischer-Speier esterification).** This reaction is reversible and hence the rate of reaction can be increased by taking excess amount of carboxylic acid or alcohol or by removing water from the reaction mixture.

$$CH_3COOH + CH_3CH_2OH \xrightleftharpoons[\Delta]{\text{con. } H_2SO_4} CH_3COOCH_2CH_3 + H_2O$$

Acetic acid — Ethanol — Ethyl ethanoate (Ethyl acetate)

$$C_6H_5COOH + CH_3OH \xrightleftharpoons[\Delta]{\text{con. } H_2SO_4} C_6H_5COOCH_3 + H_2O$$

Benzoic acid — Methanol — Methyl benzoate

(iii) Formation of anhydrides : Two molecules of carboxylic acids combine in presence of strong dehydrating agent such as P_2O_5 or mineral acid, such as con. H_2SO_4, on heating gives acid anhydrides. For example,

$$2CH_3COOH \xrightarrow[\Delta]{P_2O_5} (CH_3CO)_2O + H_2O$$

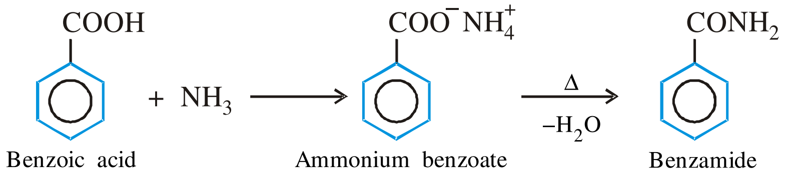
Acetic acid — Ethanoic anhydride (Acetic anhydride)

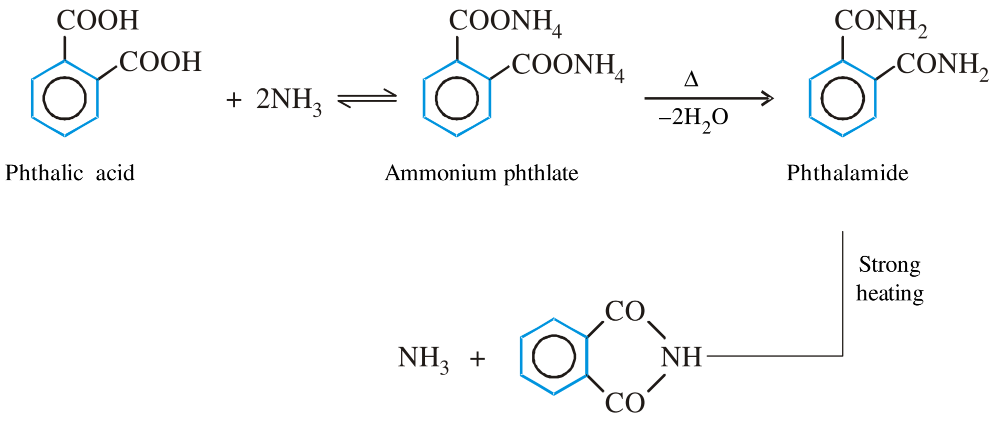
By treating acid chlorides with sodium salts of carboxylic acids, the acid anhydrides are obtained.

$$CH_3COCl + CH_3COONa \rightarrow (CH_3CO)_2O + NaCl$$

Ethanoyl chloride (Acetyl chloride) — Sodium acetate — Ethanoic anhydride (Acetic anhydride)

(iv) Formation of Amides : Carboxylic acids react with NH_3 to give ammonium salts, which on further heating at high temperature, lose a molecule of water to form amide. For example,





Phthalic acid   Ammonium phthlate   Phthalamide

Phthalimide

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \rightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow[\text{Higher temperature}]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(3) Reactions involving –COOH group as a whole :

(i) Reduction : The reduction of carboxylic acids with Lithium Aluminium hydride ($LiAlH_4$) or better with diborane (B_2H_6) gives **primary alcohol.** Using this reaction the –CO– group can be reduced to $-CH_2-$ group. For example,

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[H_2O]{\text{(i) } LiAlH_4 \text{ or } B_2H_6} \underset{\text{Ethanol } (1^0 \text{ alcohol})}{CH_3CH_2OH}$$

Diborane does not easily reduce functional groups like ester, nitro, halo etc., and sodium borohydride does not reduce the carboxyl group.

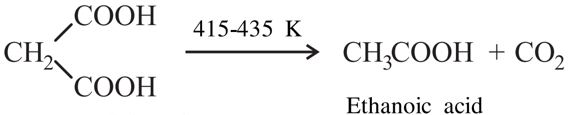
Carboxylic acid on reduction with hydroiodic acid and red phosphorus at 473 K give alkanes. In this reaction the –COOH group is reduced to $-CH_3$ group.

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + 6HI \xrightarrow[473\text{ K}]{\text{Red P}} \underset{\text{Ethane}}{CH_3\text{–}CH_3} + 2H_2O + 3I_2$$

(ii) Decarboxylation : Carboxylic acids and their salts lose carbon dioxide to form hydrocarbon and reaction is known **as decarboxylation reaction.** The sodium salts of carboxylic acid are heated with sodalime (NaOH and CaO mixture in the proportion ratio of 3:1) give alkane. e.g.,

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow{CaO / \Delta} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

If two carboxylic groups are attached to the same carbon atom called gem-dicarboxylic acid undergo decarboxylation simply on heating at 415-435 K temperature. For example,

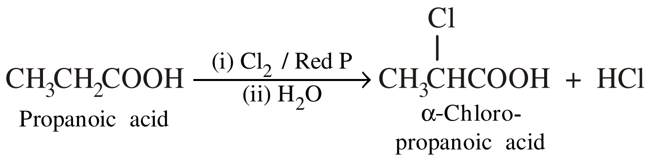


$$\underset{\text{Propanedioic acid}}{CH_2\begin{matrix} \diagup COOH \\ \diagdown COOH \end{matrix}} \xrightarrow{415\text{-}435\text{ K}} \underset{\text{Ethanoic acid}}{CH_3COOH} + CO_2$$

On electrolysis of aqueous solution of sodium or potassium salts of fatty acids at anode due to oxidation, CO_2 is liberated and alkane having double carbon is obtained. At cathode H_2 gas liberated and this process is called **Kolbe's electrolytic reduction or electrolytic decarboxylation.**

(4) Substitution reactions in the hydrocarbon part of carboxylic acids :

(i) Halogenation : Carboxylic acid having an α-hydrogen atoms are halogenated at the α-position on treatment with dichlorine or dibromine in the presence of small amount of red phosphorus to give α-halocarboxylic acid. This reaction is known as **Hell-Volhard-Zelinsky reaction.** For example,

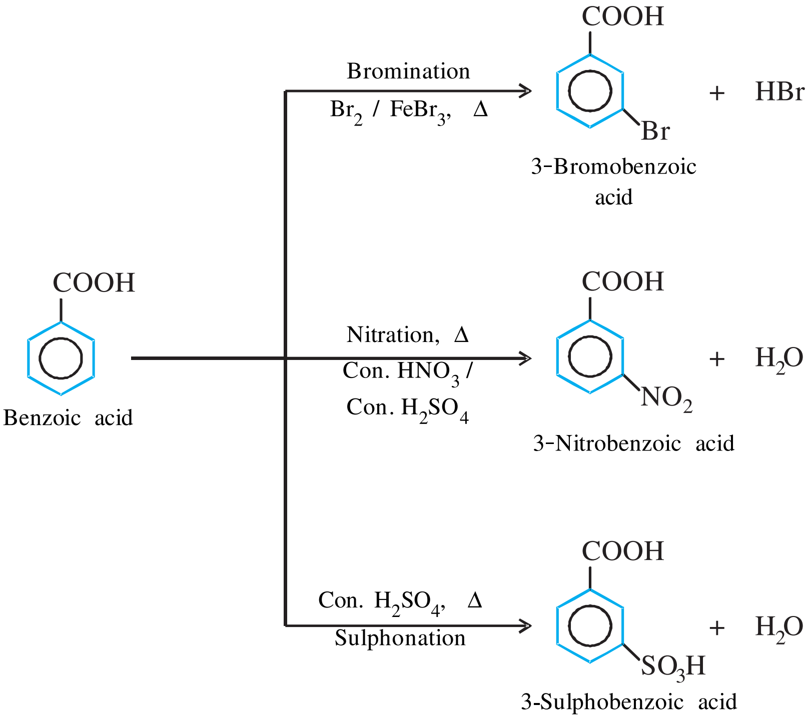


$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2 \text{ / Red P}} \underset{\substack{\alpha\text{-Chloro-}\\ \text{propanoic acid}}}{CH_3\overset{\overset{\displaystyle Cl}{|}}{C}HCOOH} + HCl$$

If more than one mole of Cl_2 or Br_2 are used then the 2nd and 3rd α-hydrogen atoms are successively substituted. For example,

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[H_2O,\ -HCl]{Cl_2 \text{ /Red P}} \underset{\substack{\text{Chloro ethanoic}\\ \text{acid}}}{ClCH_2COOH} \xrightarrow[H_2O,\ -HCl]{Cl_2 \text{ Red P}} \underset{\substack{\text{Dichloro}\\ \text{ethanoic acid}}}{Cl_2CHCOOH} \xrightarrow[H_2O,\ -HCl]{Cl_2 \text{ Red P}} \underset{\substack{\text{Trichloro}\\ \text{ethanoic acid}}}{Cl_3CCOOH}$$

(ii) Ring substitution : Aromatic carboxylic acids undergo the electrophilic substitution reactions like halogenation, nitration and sulphonation. Since the –COOH group acts as a deactivating and hence **m-directing group, so the reactions take place only under vigorous conditions.** The –COOH group deactivates the benzene ring and catalyst aluminium chloride (Lewis acid) gets bonded to the carbonyl group. So they do not undergo Friedel-Carfts reactions.

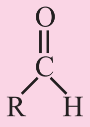


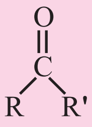
5.12 Uses of Carboxylic Acids

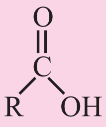
Methanoic acid is used in leather industry, rubber industry, in medicine, in dyeing and electroplating industry, Ethanoic acid is used as coagulant for latex, manufacturing of plastic, rayon and silk. It is also used as a solvent in laboratory and as vinegar in the manufacturing of pickles in food industry. Hexanedioic acid is used in manufacturing of nylon 6,6. Benzoic acid is used in medicine as urinary antiseptic and for making aniline blue in dye industry, and sodium benzoate as food preservatives. Higher fatty acids are used for manufacturing of soaps and detergents. Benzene-1,2-dicarboxylic acid is used in the manufacturing of resins and benzene-1,4-dicarboxylic acid is used in manufacturing of polyesters.

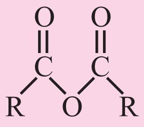
SUMMARY

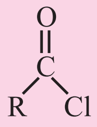
Organic compounds containing carbon-oxygen double bond ($>C=O$) are called carbonyl group or carboxyl group compounds. In aldehydes, the carbonyl group is attached to one hydrogen atom and one alkyl (or aryl or hydrogen atom) group, while in ketones it is attached to one alkyl and one aryl group or to two alkyl (or aryl) groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as carboxylic acids. In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group the compounds are known as esters, but if it is substituted by acyl group, the compounds are known as acid anhydrides. If the carbonyl group is attached to chlorine and to amino group the compounds are known as acid chlorides and amides respectively. The general formula of these compounds are expressed as

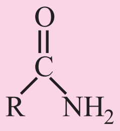

Aldehyde

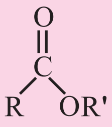

Ketone


Carboxylic acid

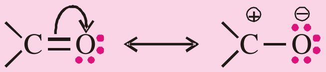

Anhydride


Acid chloride


Amide


Ester

- Aldehydes and ketones have same general molecular formula $C_nH_{2n}O$ but different functional groups like aldehydes and ketones. Therefore they are called functional groups isomers. e.g., C_3H_6O can be CH_3CH_2CHO and CH_3COCH_3 i.e. aldehyde and ketone respectively.
- Carbonyl carbon atom is sp^2 hybridised and form three σ bonds and one π bond. All the three σ-bonds lie in same plane having angle 120^0. The π-bond lies both above and below the C–O σ bond. Thus the carbonyl carbon and oxygen atoms are directly bonded to the carbonyl carbon which lie in one plane, and is confirmed by electron diffraction and spectroscopic studies.
- Due to higher electronegativity of oxygen atom relative to carbon atom the carbonyl group is polarized and carbonyl carbon becomes electrophile (Lewis acid) and oxygen becomes nucleophile (Lewis base). Carbonyl group is polar in nature and has dipole moments. Aldehydes and ketones have dipole moments 2.3-2.8 D. The resonance structures are as shown below :



- The common names of aldehydes are obtained by replacing the terminal -'ic acid' by 'aldehyde' from the common name of the corresponding carboxylic acid.
- Formic acid, acetic acid and benzoic acid the corresponding aldehydes are formaldehyde, acetaldehyde and benzaldehyde respectively.
- In the substituted aldehydes, the positions of the substituents are indicated by Greek alphabets α, β, γ, δ etc. with the carbon atom next to the –CHO group designated as α

- The IUPAC names of open chain aliphatic aldehydes are derived from the names of the corresponding hydrocarbon by replacing the terminal alphabet 'e' from its name by -'al' like methanal, ethanal etc.
- The position of substituents are indicated by numbers. The numbering of the substituents are done in such a way that the aldehyde group at the end of the chain gets number 1.
- Names of aliphatic cyclic aldehydes are given by adding suffix carbaldehyde after the full name of the cycloalkane.
- Name of aromatic aldehydes are given as benzene carbaldehyde (or benzaldehyde) and the position is indicated by numbering starting from the carbon having –CHO group.
- More than two –CHO groups are named as derivatives of the hydrocarbon which do not include the carbon atoms of the functional group.
- The common and IUPAC names of aldehydes are given in table 5.1 in the unit.
- The common names of the aliphatic and aromatic ketones are obtained by naming the two alkyl or aryl group (in the alphabetical order) attached to the ketone group as two separate words and adding suffix ketone.
- If both attaching groups are same the prefix di is used.
- The IUPAC names of ketones are derived from the name of corresponding hydrocarbon by replacing the terminal alphabet-'e' by the suffix -'one'.
- For substituted ketone the positions of the substituents are indicated by numbering the chain in such a way that the ketone group gets the lowest number.
- The common and IUPAC names of the ketones are given in table 5.2.
- The polar carbonyl groups have dipole-dipole interaction between opposite ends of the $>C=O$ group dipoles and hence due to weak intermolecular attraction the melting points and boiling points of aldehydes and ketones are higher than corresponding non-polar compounds.
- The order of boiling points is carboxylic acid > alcohol > isomeric ketone > isomeric aldehyde>ether>hydrocarbon.
- Due to hydrogen bonding with water molecules the aldehydes and ketones upto three carbon are soluble in water.
- The aromatic aldehydes and ketones due to presence of larger hydrocarbon parts (like benzene ring etc.), are insoluble in water.
- All adehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohols, chloroform etc.

- Due to presence of hydrogen atom, the carbonyl group of aldehyde is much more reactive than ketone.
- Aldehydes and ketones undergo nucleophilic addition reaction because the carbonyl carbon atom is slightly positively charged.
- In nucleophilic addition reaction the first step is reversible and also slow, so it a rate determining step. The second step is reversible.
- Due to steric effect and inductive effect the aldehydes are more reactive than ketones.
- Most of the aldehydes and aliphatic methyl ketones, due to less steric hindrance are more reactive.
- Aldehydes and ketones react with $NaHSO_3$ and give bisulphite addition product which are usually crystalline solids. On hydrolysis they give original aldehydes and ketones, so this reaction is useful for separation and purification of aldehydes and ketones.
- Addition of HCN and Grignard reagent to the aldehyde and ketone which give α-hydroxy carboxylic acid and 1^0, 2^0, 3^0 alcohols respectively.
- Addition of alcohol to aldehyde give hemiacetal and further acetal, while ketone give the same product.
- Nucleophilic addition reaction of aldehydes and ketones with NH_3 and its derivatives ($H_2N–Z$) and reaction catalysed by acids.
- Aldehydes and ketones on reduction give 1^0 and 2^0 alcohols respectively.
- Aldehydes and ketones can be reduced to hydrocarbon by using different reactions like Wolff-Kishner reduction, Clemmensen reduction and reagents like red phosphorus and HI and reduction with magnesium amalgam and water give the product-hydrocarbon.
- Oxidation of aldehydes : Tollens' test, Fehling's test and Benedict's test give the product carboxylic acid. Fehling's test and Benedict's test are not given by aromatic aldehydes.
- Oxidation of ketones by strong oxidizing agents like con. HNO_3, $KMnO_4$ / H_2SO_4, $K_2Cr_2O_7$ / H_2SO_4 give mixture of carboxylic acids.
- Oxidation of aldehydes and ketones containing CH_3CO-group give iodoform test.
- Aldol condensation and cross aldol condensation are the reactions given by aldehydes and ketones having α-hydrogen atom or atoms using dilute alkali as catalyst.
- Cannizzaro reaction is given by aldehydes and ketones which do not have an α-hydrogen atom by using con. NaOH or 50 % NaOH.
- Electrophilic substitution reactions of aromatic aldehydes and ketones are nitration, sulphonation and halogenation.
- Aldehydes and ketones are used in different fields.

- The carboxylic acids contain –COOH group, contain carbonyl and hydroxyl group so by combining the 'carb' and 'oxyl', the –COOH is called carboxyl group.
- The common names of some aliphatic carboxylic acids are derived from the Greek or Latin names of their natural sources (plant or animal products) from which they were first isolated.
- The IUPAC names of monocarboxylic acids are given by replacing the ending alphabet 'e' in the name of corresponding hydrocarbon with suffix "-ioc acid."
- For naming substituted and branched acids, the longest chain having carboxylic acid group is selected and number one is assigned to carboxylic carbon; then the successive number are assigned to carbon of the chain and the substitution is expressed.
- The IUPAC names of aromatic monocarboxylic acids are derived from benzene carboxylic acid (Benzoic acid) and the position of the substituents are indicated by number with carbon atom carrying –COOH group being number one.
- In aliphatic dicarboxylic acids, the position of –COOH group is not indicated, but in aromatic dicarboxylic acid and other (tri, tetra…poly) carboxylic acid, it is indicated by number before the multiplicative prefix and the ending -'e' of the hydrocarbon is retained.
- The common and IUPAC names of some carboxylic acids are given in table 5.5.
- The –COOH group is represented as a resonance hybrid of the three resonating structures.
- **Carboxylic acids are prepared from :**
  - → Primary alcohol and aldehyde
  - → Alkyl benzene and alkenes
  - → Nitriles and amides.
  - → Grignard reagents
  - → Acid (chloride) halide and anhydrides
  - → Esters
- Carboxylic acid in aqueous solution form intermolecular hydrogen bonding with water molecules.
- Carboxylic acids are cyclic dimer in vapour phase or in aprotic solvents.
- Carboxylic acids are stronger acids than phenol and alcohols.
- For convenience the strength of an acid is generally indicated by its pK_a value rather than its K_a value.

  $pK_a = -\log K_a$
- The acidic strength of carboxylic acids depends on the effect of various substituents like

→ effect of electron-donating group

→ effect of electron withdrawing group

→ attachment of phenyl or vinyl group directly to carbonyl group.

- The reactions of carboxylic acid are

→ Reactions involving cleavage of O–H bond.

→ Reactions involving cleavage of C–OH bond

→ Reactions involving –COOH group

- Substitution reaction in hydrocarbon part of carboxylic acid are halogenation and ring substitution as bromination, nitration and sulphonation.
- Carboxylic acids are used in different fields.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) Which of the following compounds has highest boiling point ?

(A) propanoic acid (B) propanol (C) propanone (D) propanal

(2) Which of the following compounds has highest solubility in water ?

(A) pentanone (B) butanone (C) formaldehyde (D) propanone

(3) Which of the following compounds has highest reactivity in nucleophilic addition reaction ?

(A) propanone (B) methanal (C) ethanal (D) butanone

(4) Propanone + NH_2NH_2 + KOH $\xrightarrow[\Delta]{\text{Ethylene glycol}}$?

(A) propanal (B) propanol (C) propene (D) propane

(5) Ethanol + $KMnO_4$ → ?

(A) ethanal (B) ethanoic acid

(C) ethane (D) potassium ethanoate

(6) tert-butyl benzene $\xrightarrow[\text{(ii) dil. } H_2SO_4]{\text{(i) } KMnO_4 \text{ / KOH, } \Delta}$?

(A) tert-butyl benzoic acid (B) benzoic acid

(C) tert-butanol (D) No reaction.

(7) But-2-ene $\xrightarrow[\text{(ii) dil } H_2SO_4]{\text{(i) } KMnO_4 \text{ / KOH, } \Delta}$?

(A) butanoic acid (B) ethanoic acid (C) butanol (D) ethanol

(8) Ethane nitrile $\xrightarrow[\Delta]{[H^+]\text{ or }[OH^-]}$?

(A) ethanol (B) ethanal (C) ethanoic acid (D) ethene

(9) Ethylbenzoate + NaOH $\rightarrow$?

(A) benzoic acid (B) benzene

(C) benzaldehyde (D) potassium benzoate

(10) Which of the following acids has highest relative acid strength ?

(A) acetic acid (B) propanoic acid

(C) isopropanoic acid (D) benzoic acid.

(11) Acetyl chloride + sodium acetate $\xrightarrow[\Delta]{}$

(A) ethyl acetate (B) ethyl chloride

(C) acetic anhydride (D) ethanol

(12) Sodium acetate + Sodalime $\xrightarrow{\Delta}$?

(A) acetic acid (B) ethane (C) methane (D) ethanal

(13) Propanoic acid $\xrightarrow[H_2O]{Cl_2\,/\,\text{Red P}}$?

(A) propanal (B) propanol

(C) propane (D) α-chloro propanoic acid.

(14) Which substance is used in leather industry ?

(A) methanoic acid (B) ethanoic acid (C) benzoic acid (D) pentanoic acid.

(15) Which substance is used in medicine as urinary antiseptic ?

(A) benzoic acid (B) acetic acid (C) methanoic acid (D) formic acid

2. Write the answers of the following questions in brief :

(1) Draw general structural formula of anhydride.

(2) Draw resonance structure of carbonyl group.

(3) Indicate hydrogen bonding between aldehyde and the water molecules.

(4) Write equation for reduction of methanal with $LiAlH_4$.

(5) Write the equation for Wolff-Kishner reduction of ketone.

(6) Write uses of formaldehyde.

(7) Write uses of acetaldehyde.

(8) Write uses of acetone.

(9) Draw resonance structurs of carboxylate ion.

(10) Write equation for hydrolysis of ethyl acetate.

(11) Write the reaction of formation of pinacol.

(12) Draw structure of association of carboxylic acid in liquid state.

(13) Draw dimer form of carboxylic acid in vapour state or in aprotic solvent.

(14) Draw hydrogen bonding between carboxylic acid and water molecules.

(15) Draw resonance structure of phenoxide ions.

(16) Explain pK_a in short. What does it indicate ?

(17) Write equation for reaction of acetic acid with Na_2CO_3.

(18) Write equation for acetic acid with $SOCl_2$.

(19) Write equation for heating acetic acid with P_2O_5.

(20) Write equation of nitration of benzoic acid.

(21) Write uses of methanoic acid.

(22) Write uses of benzoic acid.

(23) Write uses of ethanoic acid.

(24) Write uses of fatty acids ?

(25) Write equation of halogenation of propanoic acid.

3. Write answers of the following questions :

(1) Explain nature of carbonyl group.

(2) Explain addition of $NaHSO_3$ to aldehyde and ketone.

(3) Explain addition of HCN to aldehyde and ketone.

(4) Explain acetal formation.

(5) Explain ketal formation.

(6) Explain reduction of aldehyde.

(7) Explain Wolff-Kishner reduction.

(8) Explain Clemensen reduction.

(9) Explain Tollens' test.

(10) Explain Fehling's test.

(11) Explain Benedict's test.

(12) Explain Cannizzaro reaction.

(13) Explain preparation of carboxylic acid from 1^0 alcohol.

(14) Explain acidic nature of carboxylic acid.

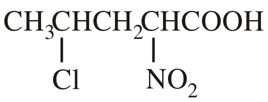
(15) Explain reduction of acetic acid.

(16) Explain decarboxylation

(17) Explain halogenation of acetic acid.

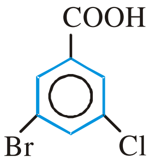
(18) Explain ring substitution in benzoic acid.

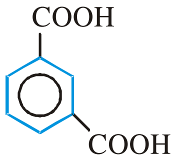
(19) Give IUPAC names :

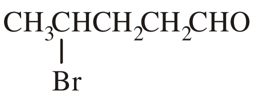
(i) 
$CH_3\underset{Cl}{CH}CH_2\underset{NO_2}{CH}COOH$

(ii) $CH_3CH_2CH_2CN$

(iii) $CH_3CH_2COOCH_2CH_3$

(iv) 

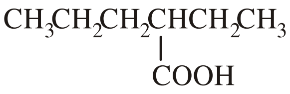
(v) 

(vi) 
$CH_3\underset{Br}{CH}CH_2CH_2CHO$

(vii) 
$CH_3CH_2\underset{Cl}{CH}COCH_2CH_3$

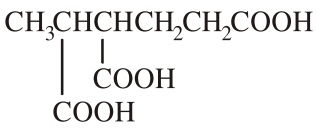
(viii) $CH_3COCH_2CH_2CH_3$

(ix) $HOOCCH_2CH_2CH_2COOH$

(x) 
$CH_3CH_2CH_2\underset{COOH}{CH}CH_2CH_3$

(xi) 
$CH_3CH_2-\overset{COOH}{CH}-CH_2CH_2COOH$

(xii) 
$CH_3CH_2\underset{Cl}{CH}\underset{Br}{CH}\underset{I}{CH}COCH_3$

(xiii) 
$CH_3\underset{COOH}{CH}\underset{COOH}{CH}CH_2CH_2COOH$

(xiv) $CH_3CH_2CH{=}CHCH_2COOH$

4. Write the answers of the following questions in detail :

(1) Explain the nucleophilic addition reactions of aldehydes and ketones.

(2) Explain the relative reactivity of aldehydes and ketones.

(3) Explain nucleophilic addition reactions followed by elimination of a molecule of water for aldehydes and ketones.

(4) Explain reduction of aldehydes.

(5) Explain oxidation of aldehydes.

(6) Explain oxidation of ketones.

(7) Explain aldol and cross aldol condensation.

(8) Explain electrophilic substitution reactions of aromatic aldehyde and ketones.

(9) Give the different methods of preparation of carboxylic acid.

(10) Explain the factors that affect the acidic strength of carboxylic acids.

(11) Explain reaction involving cleavage of C–OH bond in carboxylic acid.

(12) Explain reaction involving cleavage of O–H bond in carboxylic acid.

(13) Explain reaction involving of –COOH (as a whole) in carboxylic acid.

●

Unit

6

Organic Compounds Containing Nitrogen

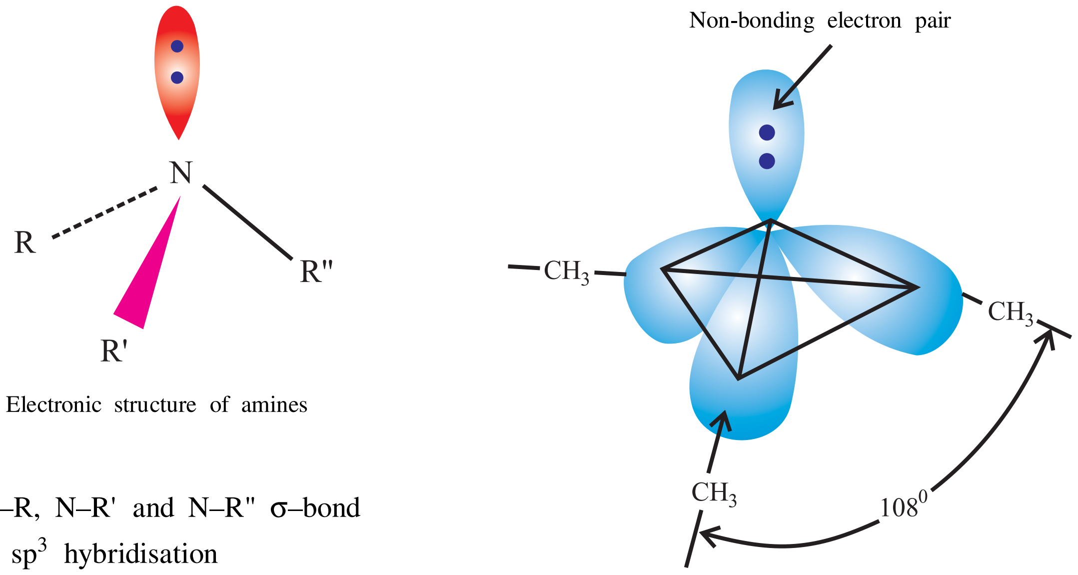
6.1 Introduction

In organic compounds the important functional groups containing nitrogen are amino, cyano or nitrile, isocyanide and nitro groups. If amino group is attached with carbon then an amino compound, is formed if cyano or nitrile group is attached then cyanide or nitrile compounds, the isocyanides group is attached then isocyanide compounds and if nitro group is attached then nitro compounds are made. In this unit, we shall study amine compounds, cyanide (nitrile) compounds, isocyanide compounds and nitro compounds.

6.2 Amines (Structure of Amine Compounds)

As the hydrogen present in water is replaced by hydrocarbon group, alcohol, phenol and ether are formed, similarly if hydrogen present in ammonia is replaced by hydrocarbon group then amine is formed. So, the structures of amine compounds are similar to structure of ammonia. **In the amine class of compounds, mainly carbon, hydrogen and nitrogen elements are present. One, two or all the three hydrogen atoms present in ammonia are displaced by alkyl or aryl groups.**

Like ammonia, in amine compounds, nitrogen atom is trivalent and possesses one nonbonding electron pair. Therefore the atomic orbital of nitrogen atom in amine compounds possess sp^3 hybridisation and the compounds possess pyramidal structure. Each sp^3 hybrid orbit of nitrogen gets overlapped with atomic orbital of carbon and forms amine compounds. The fourth orbital of nitrogen possesses nonbonding electron pair. Because of the presence of non-bonding electron pairs, C–N–R (where R is H or C) bond angle decreases slightly from $109^0\ 28'$. As shown in the fig 6.1 the bond angle in trimethyl amine is 108^0.



Electronic structure of amines

N–R, N–R' and N–R'' σ–bond

N sp^3 hybridisation

any R–N–R angle ≈ 109.5^0

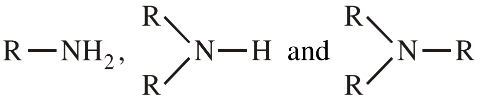
Pyramidal shape of tertiary amine

Fig. 6.1

6.3 Classification of Amine Compounds

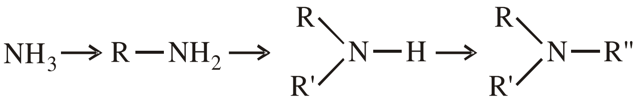
The classification of amine compounds is made on the basis of alkyl or aryl groups combined with nitrogen of amino group. If alkyl group is attached it is called alkyl amine and if aryl group is attached it is called aryl amine.

On replacement of hydrogen present in ammonia, if one alkyl or aryl group is attached with nitrogen, it is called primary (1^0) amine, if two groups are attached then secondary (2^0) and if three groups are joined, then tertiary (3^0) amine. The general formula of compounds in amino class is shown as :



$R-NH_2$, R_2N-H and R_2N-R

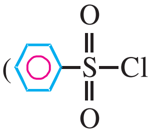
where R = alkyl or aryl group. If all the alkyl or aryl groups in amine compounds are same they are called simple amines and if different groups are there then, they are called mixed amines. Alkyl amines are called aliphatic amines and aryl amines are called aromatic amines.



$NH_3 \rightarrow R-NH_2 \rightarrow RR'N-H \rightarrow RR'N-R''$

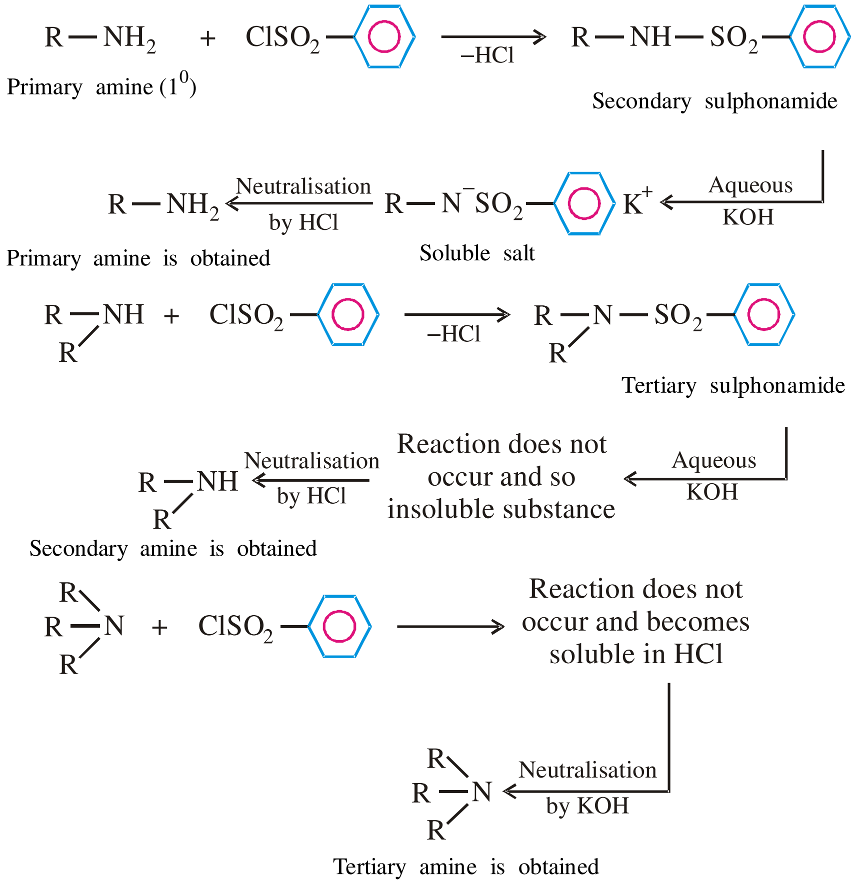
Primary (1^0) Secondary (2^0) Tertiary (3^0)

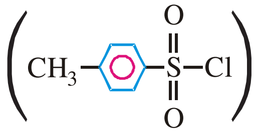
Separation of primary, secondary and tertiary amines : The separation of alkyl or aryl mixture of primary, secondary and tertiary amine can be carried out by the use of Hinsberg's reagent.

Benzene sulphonylchloride ( or $C_6H_5SO_2Cl$) is called Hinsberg's reagent.

In the mixture of primary, secondary and tertiary alkyl (aliphatic) and aryl (aromatic) amines, if benzene sulphonylchloride is added, then by the chemical reaction of primary, and secondary amine, secondary sulphonamide and tertiary sulphonamide are formed respectively; while tertiary amine does not react. To this mixture when dilute hydrochloric acid (HCl) is added the unreacted tertiary amine becomes soluble and the secondary sulphonamide and tertiary sulphonamide being insoluble in acid are obtained as residue by filtration. By neutralization of filtrate, tertiary amine is separated.

In the residue of secondary and tertiary sulphonamide, aqueous solution of potassium hydroxide (KOH) is added so that secondary sulphonamide becomes soluble. This reaction mixture is filtered and by neutralisation of the filtrate with acid, primary amine and secondary amine from residue gets separated by neutralisation.



Presently paratoluene sulphonylchloride  **is used of instead benzene sulphonylchloride.**

6.4 Nomenclature of Amine Compounds (IUPAC and Common)

For nomenclature of primary alkyl amine, after the alkyl group ‘amine’ word is placed viz. methylamine, ethylamine etc.

For common nomenclature of secondary alkyl amine, if two alkyl groups attached to nitrogen are the same then the prefix ‘di’ is placed before alkyl group followed by ‘amine’ viz dimethylamine, diethylamine etc. If the two alkyl groups attached to nitrogen are different then, the alkyl groups are arranged in the English alphabetical order and the word ‘amine’ is placed in the end. viz. ethylmethylamine, methylpropylamine etc.

For common nomenclature of tertiary amine if the three alkyl groups attached to nitrogen are same then the word tri is placed as the prefix before alkyl group and then the word ‘amine’ is placed in the end. Viz. trimethylamine, triethylamine etc. If two alkyl groups from the attached three alkyl groups are common, then the prefix di is placed before the two common alkyl groups and then the name of third alkyl group is attached and at the end the word ‘amine’ is placed viz. ethyldimethylamine, diethylmethylamine. If all the three alkyl groups attached to nitrogen are different then the alkyl groups are arranged in the English alphabetical order and then in the end word ‘amine’ is placed viz. ethylmethylpropylamine, butylethylmethylamine.

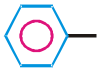
Amine compounds having more than one amine group according to the number of amino groups prefix di, tri, tetra etc. are attached. viz. $H_2N–CH_2–CH_2–NH_2$ is ethylenediamine, $H_2N–CH_2–CH(NH_2)–CH_2–NH_2$ is propylenetriamine.

IUPAC names :

(i) For IUPAC nomenclature of primary amine, the longest carbon chain of original hydrocarbon is determined and then ‘e’ is removed from the name of hydrocarbon and suffix amine is applied viz. methan + amine = Methanamine, ethan + amine = ethanamine, benzen + amine = benzenamine.

$CH_3–NH_2$ Methanamine

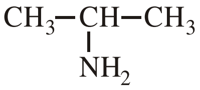
$CH_3\text{-}CH_2\text{-}NH_2$ Ethanamine


NH_2 or $C_6H_5 \cdot NH_2$ Benzenamine

It is necessary to note here that the common name of benzenamine is aniline. It is also accepted as IUPAC name.

(ii) If there are more than two carbon in primary alkylamine then in the longest carbon chain at original hydrocarbon, the position of amino group showing lowest number, suffix amine is shown earlier to it. viz. propan-1-amine, propan-2-amine.

$CH_3–CH_2–CH_2–NH_2$ Propan-1-amine

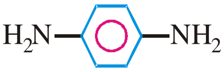

$CH_3–\underset{\displaystyle NH_2}{\underset{|}{CH}}–CH_3$ Propan-2-amine

(iii) For amine compounds having more than one carbon, in the number of amino group if it is two, three... etc. then di, tri, ... etc. are written as prefix before the ‘amine’ group, respectively **Here, the last letter ‘e’ is not removed** e.g.,

$H_2N–CH_2–CH_2–NH_2$ Ethane-1,2-diamine

$H_2N–CH_2–CH(NH_2)–CH_2–NH_2$ Propane-1,2,3-triamine

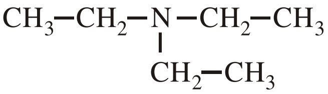
$H_2N-(CH_2)_6-NH_2$ Hexane-1,6-diamine



Benzene-1,4-diamine

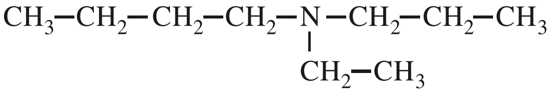
(iv) For the names of secondary and tertiary amines, the names are written according to rules (i), (ii) and (iii). Here symbol N is used to show the position of displacers of hydrogen in amine group e.g.

$CH_3-NH-CH_2-CH_3$ N-Methylethanamine



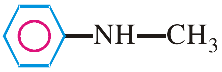
$CH_3-CH_2-N(CH_2-CH_3)-CH_2-CH_3$

N, N-Diethylethanamine

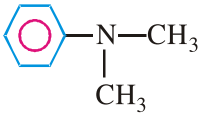


$CH_3-CH_2-CH_2-CH_2-N(CH_2-CH_3)-CH_2-CH_2-CH_3$

N-Ethyl-N-propylbutanamine



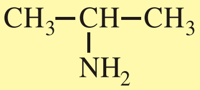
N-Methylbenzenamine

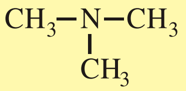
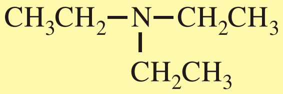
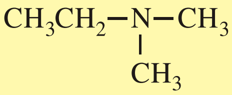
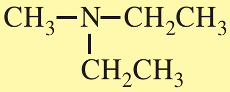
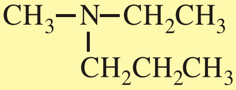
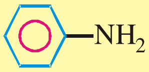
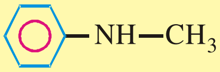
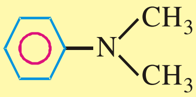


N, N-Dimethylbenzenamine

The structural formula, IUPAC name, common name, type and boiling points of certain amine compounds are given in table 6.1.

Table 6.1 Amine compounds

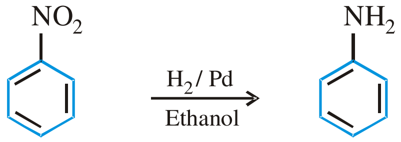
Sr.	Structural formula	Common name	IUPAC name	Type	Boiling point
1.	CH_3NH_2	Methylamine	Methanamine	1^0	280 K
2.	$CH_3CH_2NH_2$	Ethylamine	Ethanamine	1^0	290 K
3.	$CH_3CH_2CH_2NH_2$	Propylamine	Propan-1-amine	1^0	322 K
4.	 $CH_3-CH(NH_2)-CH_3$	Isopropylamine	Propan-2-amine	1^0	306 K
5.	$CH_3-NH-CH_3$	Dimethylamine	N-Methylmethanamine	2^0	280 K
6.	$CH_3CH_2-NH-CH_2CH_3$	Diethylamine	N-Ethylethanamine	2^0	329.K
7.	$CH_3CH_2CH_2-NH-CH_2CH_2CH_3$	Dipropylamine	N-Propylpropan-1-amine	2^0	383 K

8.	$CH_3-NH-CH_2CH_3$	Ethylmethylamine	N-Methylethanamine	2^0	309 K
9.	$CH_3-NH-CH_2CH_2CH_3$	Methylpropylamine	N-Methylpropan-1-amine	2^0	335 K
10.	 $CH_3-\underset{\substack{\vert\\CH_3}}{N}-CH_3$	Trimethylamine	N, N-Dimethyl methanamine	3^0	276 K
11.	 $CH_3CH_2-\underset{\substack{\vert\\CH_2CH_3}}{N}-CH_2CH_3$	Triethylamine	N, N-Diethyl ethanamine	3^0	363 K
12.	 $CH_3CH_2-\underset{\substack{\vert\\CH_3}}{N}-CH_3$	Ethyldimethylamine	N, N-Dimethyl ethanamine	3^0	310 K
13.	 $CH_3-\underset{\substack{\vert\\CH_2CH_3}}{N}-CH_2CH_3$	Diethylmethylamine	N-Ethyl-N-methyl ethanamine	3^0	339 K
14.	 $CH_3-\underset{\substack{\vert\\CH_2CH_2CH_3}}{N}-CH_2CH_3$	Ethylmethylpropyl-amine	N-Ethyl-N-methyl propan-1-amine	3^0	367 K
15.		Aniline	Benzenamine or aniline	1^0	475 K
16.		N-Methylaniline	N-Methylbenzenamine	2^0	469 K
17.		N, N-Dimethylaniline	N, N-Dimethyl benzenamine	3^0	467 K

6.5 Preparation of Amine Compounds

The methods for preparation of amine compounds are as follows :

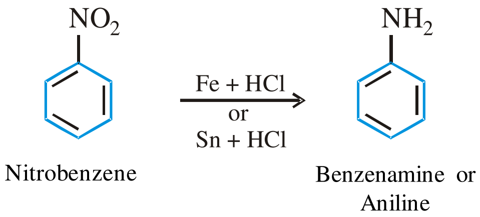
(i) Reduction of nitro compounds : Amine is produced by reduction reaction of nitro compounds by passing dihydrogen gas in presence of catalyst like nickel, palladium or platinum. Amine is also produced by their reduction in presence of metal in acidic medium. By reduction of nitroalkanes, alkanamines are formed. **In reduction of nitroalkane $LiAlH_4$ or $NaBH_4$ is also used.**



Nitrobenzene Benzenamine or aniline

$$CH_3-CH_2-NO_2 \xrightarrow[\text{or } NaBH_4]{LiAlH_4} CH_3-CH_2-NH_2$$

Nitroethane Ethanamine



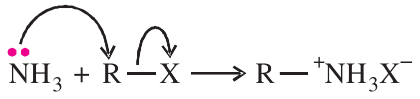
Nitrobenzene

Benzenamine or Aniline

Presently, iron scrap and hydrochloric acid is used in larger proportions.

(ii) Ammonolysis of halides : As studied earlier in semester III, the carbon-halogen bond which is present in alkyl or aryl halide is easily broken by nucleophilic reagent. Hence by reaction of ethanolic ammonia on alkyl or aryl halide, the nucleophilic reagent (NH_2) substitutes the halogen and amine is formed. **The C–X bond is broken by molecule of ammonia so the reaction is called ammonolysis.**

The ammonolysis reaction of alkyl halide is carried out in air tight tube at 373 K temperature. Primary amine is first obtained, then it reacts with alkyl halide by chain reaction and secondary and tertiary amines are formed. In the end quarternary ammonium salt is formed.



$$\ddot{N}H_3 + R-X \longrightarrow R-\overset{+}{N}H_3X^-$$

By the reaction of ammonium salt with strong base free amine is obtained.

$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \rightarrow R-NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

$$\underset{\substack{(1^0)\\ \text{Primary}}}{R-NH_2} \xrightarrow{RX} \underset{\substack{(2^0)\\ \text{Secondary}}}{R_2NH} \xrightarrow{RX} \underset{\substack{(3^0)\\ \text{Tertiary}}}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quarternary}\\ \text{ammonium salt}}}{R_4\overset{+}{N}-\overset{-}{X}}$$

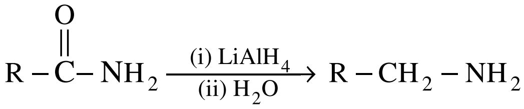
The disadvantage of ammonolysis is that the mixture of primary, secondary, tertiary and quarternary salt is obtained as product but by the use of ammonia in larger proportion primary amine can be obtained.

The order of reactivity of halide with amines is RI > RBr > RCl

(iii) Reduction of nitrile : By reaction of nitrile with lithium aluminium hydride ($LiAlH_4$) or by catalytic hydrogenation reaction, reduction takes place and primary amine is obtained. **This reaction is useful in increasing the number of carbons in the amine series i.e.** reaction of amine with one carbon can be started for preparation of amines.

$$R-C\equiv N \xrightarrow[Na(Hg)\,/\,C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

(iv) Reduction of amide : Amines are obtained by reduction of amide with lithium aluminium hydride.

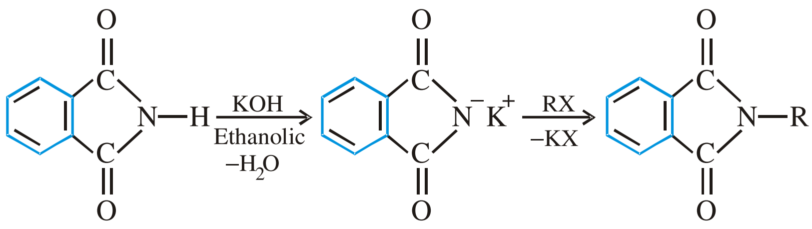


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R-CH_2-NH_2$$

Amide

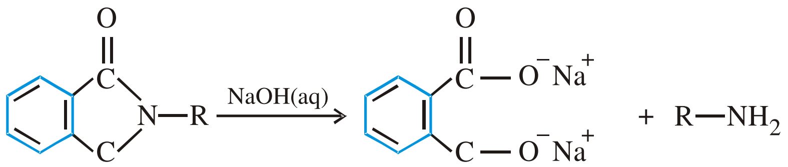
Amine

(v) Gabriel pthalimide synthesis : Gabriel synthesis is used in the preparation of primary amines. By reaction of pthalimide with ethanolic potassium hydroxide, potassium salts of pthalimide are obtained which are when heated alkyl halide primary amines are obtained by alkaline aromatic hydrolysis. Primary aromatic amine can not be prepared by this method beacuse nucleophilic aryl halide, does not become favourable anion for phthalimide.



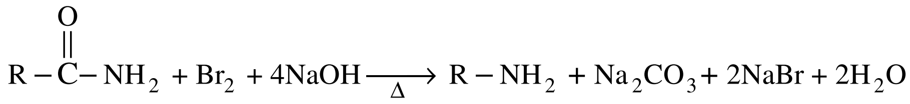
Pthalimide

N-Alkyl pthalimide



Primary amine

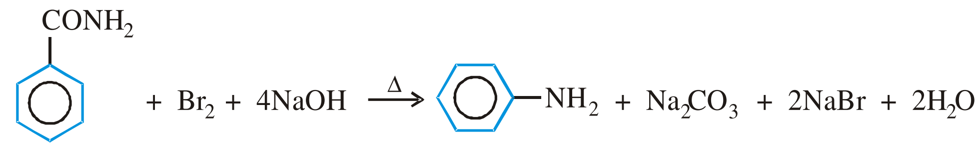
(vi) Hoffmann reaction : In Hoffmann reaction to prepare primary amine, the amide is heated with ethanolic solution of sodium hydroxide so that during the decomposition reaction, in place of carbonyl carbon in amide the nitrogen atom migrates to alkyl or aryl group. **Primary amine having one carbon less than amide is thus obtained.**



$$R-\overset{\overset{\large O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\Delta]{} R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Ethanamide　　　　Methanamine

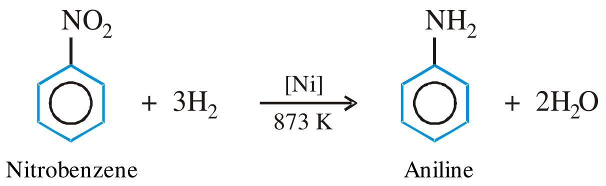


Benzenamide

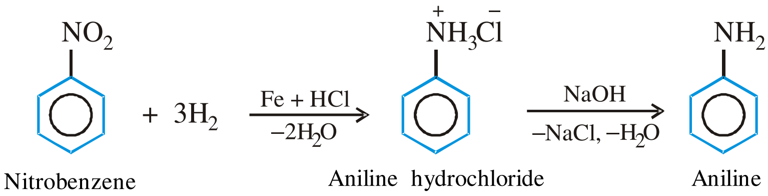
Aniline or Benzenamine

Industrial production of Aniline : As the use of aniline is widespread in chemical industry, its industrial production is carried out by reduction of nitrobenzene or by ammonolysis reaction with chlorobenzene.

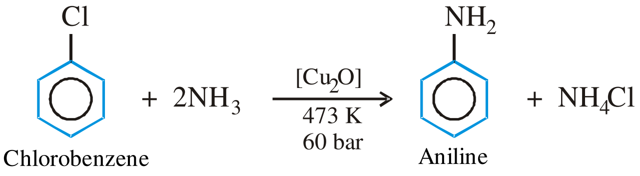
(a) The mixture of vapour of nitrobenzene and dihydrogen gas is heated at 873 K in presence of nickel catalyst, aniline is formed by reduction. Pure aniline is obtained by this method.



(b) By reduction of nitrobenzene with iron and hydrochloric acid, aniline hydrochloride is formed which is neutralised with sodium hydroxide and so aniline is separated.



When the mixture of chlorobenzene and two moles of ammonia are heated at 60 bar pressure and 473 K temperature in closed vessel in presence of Cu_2O catalyst, aniline is produced by ammonolysis reaction.



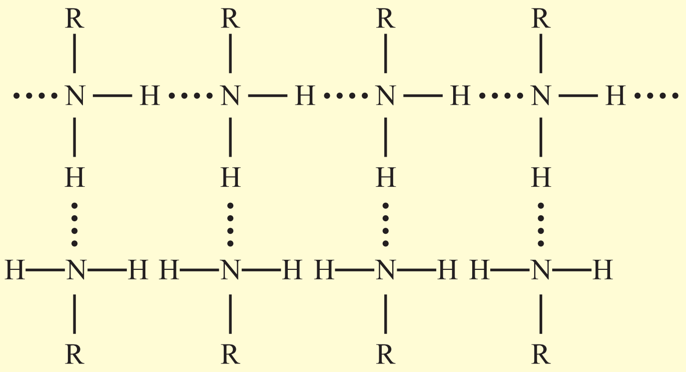
Pure aniline is almost colourless liquid having bad smell. It becomes dark red coloured when kept open in air for a long time because of oxidation. **The industrial use of aniline is in the manufacture of drugs, resin, varnish, as well as solvent and in vulcanisation of rubber.**

6.6 Physical Properties of Amines

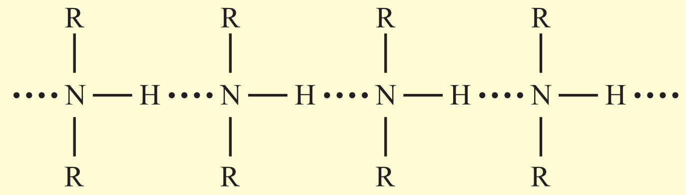
The boiling points of the primary amines having same number of carbon atoms containing alkane are higher; also the boiling points increases successively with the increase in number of carbon atoms in primary amine viz, in methanamine (boiling point 280 K), ethanamine (boiling point 290 K) propanamine (boiling point 322 K) increases successively with the increase in number of carbon atoms. In the isomeric alkyl amines having same molecular formula, the boiling point decreases from primary amine to tertiary amine, viz. (1^0) Propanamine (boiling point 322 K), (2^0) ethylmethyl amine (boiling point 309 K) and (3^0) trimethyl amine (boiling point 276 K) boiling points are decreasing.

As the electronegativity of nitrogen is less than that of oxygen, the $N^{-\delta}–H^{+\delta}$ bond in amines is less polar than the $O^{-\delta}–H^{+\delta}$ bond in alcohol. Hence, amine compounds are more polar than alkane but less polar than alcohol. Also, the intermolecular attraction in amine is less than that in alcohol. Hence, the boiling points of amine are higher than those of their corresponding alkanes and lower than those of their corresponding alcohols, viz ethanamine (boiling point 290 K) is more than ethane (boiling point 184 K) but lower than ethanol (boiling point 351 K).

There are intermolecular hydrogen bonds in primary and secondary amines while they are not there in tertiary amine. Hence, in isomeric primary alkyl amines having same molecular formula, it is highest, in secondary amine it is comparatively less and it is least in tertiary amine. viz. in (1^0) propanamine, (2^0) ethylmethylamine and (3^0) trimethylamine there is decrease in boiling point which is shown in fig 6.2.



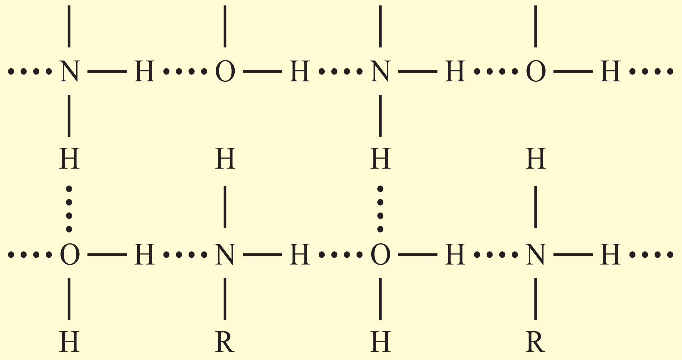
Intermolecular hydrogen bond between molecules of 1^0 amine



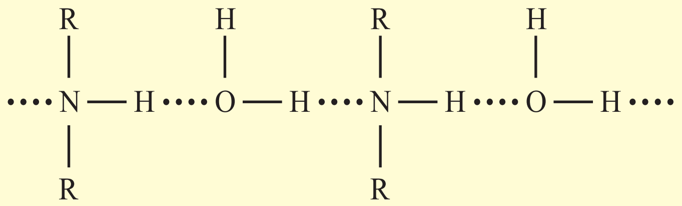
Intermolecular hydrogen bond between molecules of 2^0 amine

Fig. 6.2

In the aqueous solutions of primary and secondary amine compounds, water and amine molecules form hydrogen bond so the intermolecular attraction increases. In primary amines, there are two hydrogen atoms on the nitrogen and in secondary amine one hydrogen atom on nitrogen so the number of hydrogen bonds in primary amine becomes double. Hence, secondary amines corresponding to their primary amines having less molecular mass are less soluble in water as shown in the Fig 6.3.



Intermolecular hydrogen bond between molecules of 1^0 amine and water



Intermolecular hydrogen bond between molecules of 2^0 amine and water

Fig. 6.3

6.7 Chemical Reactions of Amine Compounds

(1) Basic characteristics of amine compounds : In amine compounds, the nitrogen atom has a non bonding electron pair, so amine compounds behave as Lewis base. **As amine compounds possess basic property, they react with acid and form salts.**

$$R-\ddot{N}H_2 + HX \rightleftarrows R-\overset{+}{N}H_3\overset{-}{X} \text{ (Salt)}$$

These amine salts are soluble in water but insoluble in organic (non polar) solvents like ether. By reaction of amine salts with base like NaOH, the original amine compound is obtained back.

$$R-\overset{+}{N}H_3\overset{-}{X} + OH^- \rightarrow R-\ddot{N}H_2 + H_2O + \overset{-}{X}$$

The strength of amines as base can be explained easily as follows according to K_b or pK_b values.

$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + OH^-$$

$$K = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$

$$K\,[H_2O] = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$\therefore\ K_b = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]} \quad \text{or} \quad pK_b = -\log K_b$$

Higher value of K_b (or lower value of pK_b) shows more basicity of amine. In table 6.2 the values of pK_b of some amine compounds are shown. For ammonia the value of pK_b is 4.75. The values of pK_b of aliphatic amines are between 3 to 4.22 and so they are a stronger base than ammonia; while the values of pK_b of aromatic amines are higher than 4.22, and so they are weak base.

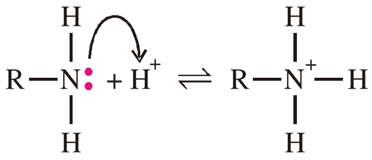
Table 6.2 pK_b values of aqueous solution of amines

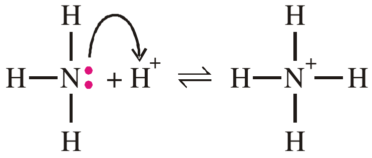
Sr.	Name of amine	pK_b
1.	Methanamine	3.38
2.	N-Methylmethanamine	3.27
3.	N, N-dimethylmethanamine	4.22
4.	Ethanamine	3.29
5.	N-Ethylethanamine	3.00
6.	N, N-Diethylethanamine	3.25
7.	Benzenamine	9.38
8.	Phenylmethanamine	4.70
9.	N-Methylaniline	9.70
10.	N, N-Dimethylaniline	8.92

Relation between basicity of amines and structure : The basicity of amines is related with their structures. The basicity of amine depends on the tendency to form positive ion easily by receiving proton from acid. If the corresponding positive ion of amine is more stable then, amine is more basic.

(a) Basicity of aliphatic amine (alkanamine) :

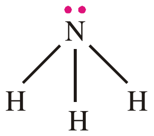
(i) Comparison of alkanamine with ammonia : The basicities of alkanamies and ammonia are compared by taking into consideration their reaction with proton (H^+).



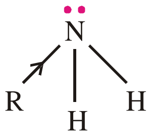


Because of the electron donating property of alkyl group, in alkanamine, alkyl group produces + I effect (You have studied + I effect in semester I). Hence, in alkalanine the non-bonding electron pair is easily available for sharing with proton. In addition, they attain stability because of + I effect of alkyl group, the **displaced ammonium ion formed from amine by, spreading of positive charge. Hence, alkanamines are stronger base than ammonia.**

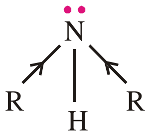
(ii) Comparison of primary, secondary and tertiary alkanamines : Going from tertiary amine to primary amine, the + I effect of alkyl group is decreasing because of the three groups attached with nitrogen atom in primary, secondary and tertiary amines having one, two and three alkyl groups are attached respectively.



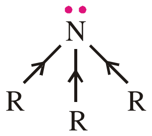
Ammonia



Primary Amine



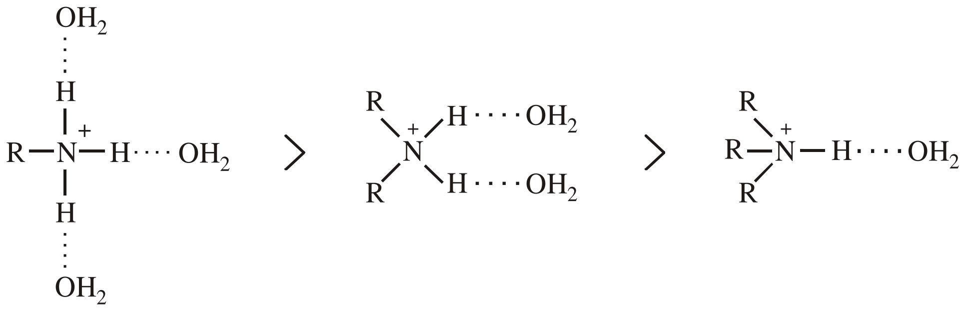
Secondary Amine



Tertiary Amine

Alkyl group is electron releasing group and so it sends the electrons of bond towards N. Thus the electron density of N-atom increases. As there are more number of alkyl group in tertiary amine, N atom will have more electron density in the compound. So such compounds can easily donate electron pair. **Hence, the order of basicity of ammonia, primary amine, secondary amine and tertiary amine gaseous phase is Tertiary amine > secondary amine > primary amine > ammonia.**

The strength of different types of alkanamines in aqueous medium are not observed in the above order, because in addition to + I effect of alkyl group due to the solvation (hydration) with molecule of water, the stability of displaced positive ion affect the stability. More the size of the positive ion less is the solvation. Hence the stability of positive ion is less. The order of stability of different positive ions in aqueous medium is as below :



So the order of basicity of alkanamines will be primary amine > secondary amine > tertiary amine.

Also, if the alkyl group is small (viz. $-CH_3$) then there is no steric hindrance for H–bond but for alkyl group bigger than $-CH_3$ (viz. $-C_2H_5$). If $-C_2H_5$ is present then the steric hindrance increases and so there is a difference in basic strength. Thus, +I effect, solvation effect and steric hindrance of alkyl group play an important role in determining the strength of alkanamine as base in aqueous medium.

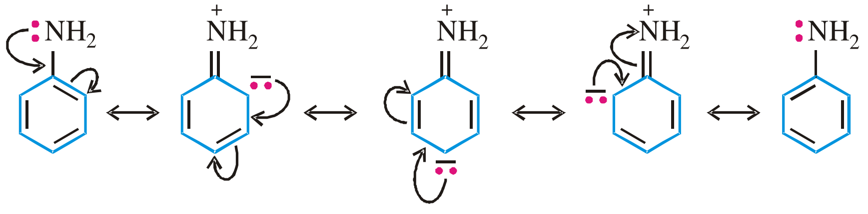
The order of strength as base in methyl displaced amines and ethyl displaced amines is respectively as follow :

$(C_2H_5)_2{-}NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ and

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

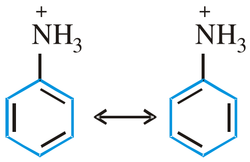
(b) Basicity of aromatic amine (Aryl amine) :

(i) The basicity of aryl amine is less than that of ammonia because of the resonance of aniline as follows : the non-bonding electron pair on N delocalises on benzene ring. Hence, the non-bonding electron pair is not easily available for protonation on N.



(I) (II) (III) (IV) (V)

Also, the anilinium ion that is obtained by protonation of aniline possesses two resonance structures.



So, the stability of aniline is more than anilinium ion. Hence, the tendency of aniline or aromatic amine to receive proton is less.

The resonance structures are not available in ammonia and aliphatic amine compounds, like aniline, so the electron pair on their N atom is localised. Hence, these compounds can easily donate electron pairs so that their basicity is more than that of aniline. As discussed in the earlier points, keeping in mind the order of basicity of aliphatic amine and ammonia the order of basicity of amine compounds can be written as follows :

Tertiary amine > secondary amine > primary amine > ammonia > aniline.

(ii) In the case of substituted aniline, it is found that because of the presence of electron donating groups like $-OCH_3$, $-CH_3$ the strength as base increases. While because of the presence of electron attracting groups like $-NO_2$, $-SO_3H$, $-COOH$ its strength as a base decreases.

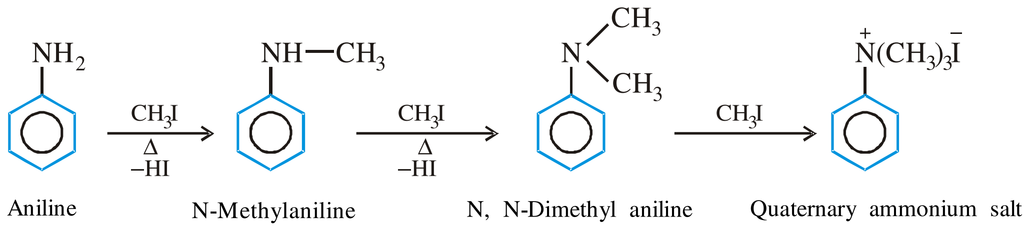
(2) Alkylation : By reaction of aliphatic and aromatic primary (1^0) amines with alkyl halide, secondary (2^0) amine is obtained. If it reacts with more amount of alkyl halide, then successively tertiary and then quarternary ammonium salt is obtained.

(a) On reacting ethanamine with ethyl iodide, N-ethylethanamide is obtained. By reacting this product with more amount of ethyl iodide, first N, N-diethylethanamine and then tetramethyl ammonium iodide salt is obtained

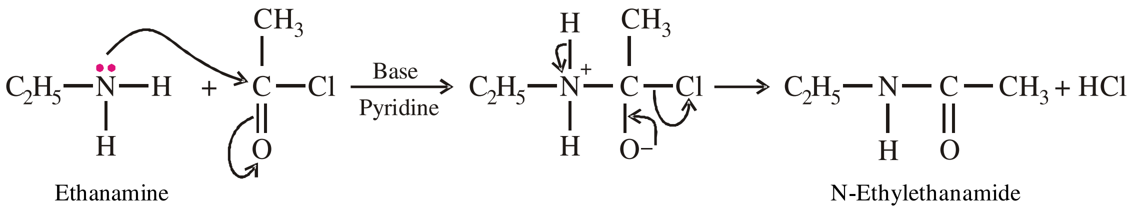
$$C_2H_5NH_2 + C_2H_5I \xrightarrow[-HI]{} (C_2H_5)_2NH \xrightarrow[-HI]{+C_2H_5I} (C_2H_5)_3N \xrightarrow{+C_2H_5I} (C_2H_5)_4\overset{+}{N}\overset{-}{I}$$

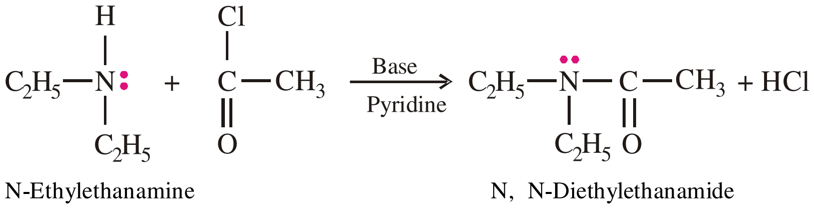
Ethanamine   N-Ethyl ethanamine   N, N-Diethyl ethanamine   Quaternary ethyl ammonium iodide (salt)

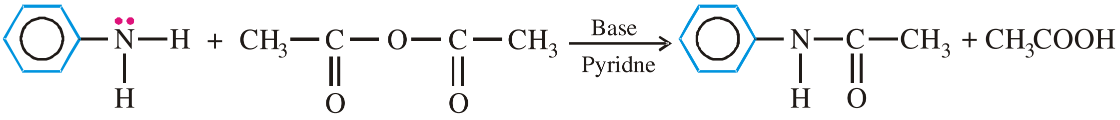
(b) Similarly, on heating aniline with methyl iodide N-Methylaniline is obtained. If methyl iodide is taken in excess proportion then tertiary amine and then quaternary ammonium salt is obtained.



(3) Acylation : When aliphatic and aromatic primary and secondary amines react with acid chloride or acid anhydride, nucleophilic subtitution reaction takes place and amide product is obtained. This reaction is known as acylation. This reaction is carried out in pyridine which is a stronger base than amine.

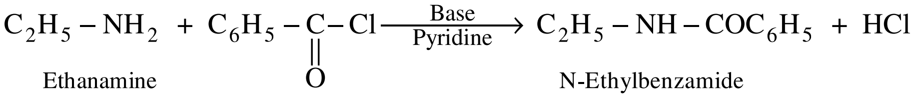






N-Phenylethanamine
(Acetanilide)

Primary and secondary amine react with benzoyl chloride. This reaction is called benzoylation.



$$C_2H_5-NH_2 + C_6H_5-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\text{Pyridine}]{\text{Base}} C_2H_5-NH-COC_6H_5 + HCl$$

Ethanamine N-Ethylbenzamide

$$C_6H_5-NH_2 + C_6H_5COCl \xrightarrow[\text{Pyridine}]{\text{Base}} C_6H_5-NH-CO-C_6H_5 + HCl$$

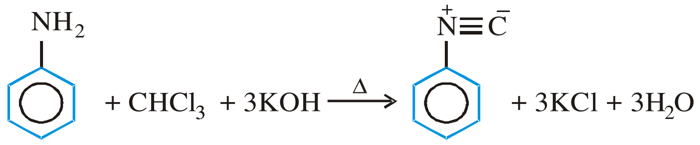
Aniline N-Phenylbenzamide

(4) Carbylamine reaction : On heating aliphatic or aromatic primary amine with chloroform ($CHCl_3$) and alcoholic potassium hydroxide (KOH) foul smell possessing poisonous isocyanide (carbylamine) is formed. This reaction is called carbylamine test or isocyanide identification. Secondary and tertiary amines do not give this test. **This test is used in laboratory for the identification of primary amine.**

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-\overset{+}{N}\equiv\overset{-}{C} + 3KCl + 3H_2O$$

$$CH_3-CH_2-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-CH_2-NC + 3KCl + 3H_2O$$

Ethanamine Ethyl isocyanide



Aniline or
Benzenamine

Phenyl isocyanide

(5) Reaction with nitrous acid : All the three types (1^0, 2^0 and 3^0) amine compounds react with nitrous acid (HNO_2) in different ways. Here, nitrous acid is prepared by the reaction of sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl)

(a) Primary alkyl amine reacts with nitrous acid (HNO_2) and gives alkyldiazonium salt which is unstable and so this salt releases nitrogen and changes to alcohol.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-\overset{+}{N_2}\bullet\overset{-}{Cl}] \xrightarrow{H_2O} R-OH + N_2 + HCl$$

Alkanamine Unstable Alcohol

$$CH_3–CH_2–NH_2 + HNO_2 \xrightarrow[+ HCl]{NaNO_2} [CH_3–CH_2–\overset{+}{N_2}\,\overset{-}{Cl}] \xrightarrow{H_2O} CH_3–CH_2–OH + N_2 + HCl$$

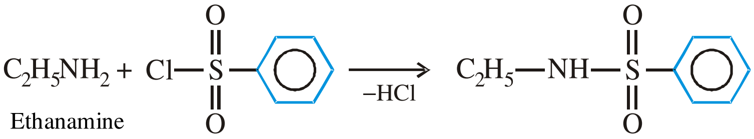
Ethanamine Unstable Ethanol

(b) Aromatic primary amine reacts with nitrous acid (HNO_2) at low temperature (273-278 K) and forms diazonium salt. The use of this salt in synthesis of aromatic compounds is very important which we shall study later on in this unit.

$$C_6H_5NH_2 \xrightarrow[\text{[HNO}_2\text{]} \ \ 273\text{-}278\text{ K}]{NaNO_2 + HCl} C_6H_5-\overset{+}{N}_2\overset{-}{Cl} + NaCl + 2H_2O$$

Benzenamine

(6) Reaction with Hinsberg reagent : Primary amine and secondary amine react with benzene sulphonyl chloride (Hinsberg reagent) and give sulphonamide product while in tertiary amine, because hydrogen is not attached with N, it does not undergo this reaction.



Ethanamine

Benzene sulphonyl chloride

N-Ethyl benzene sulphonamide (2^0)

In this compound, acidic hydrogen is combined with nitrogen, so it is soluble in alkali.

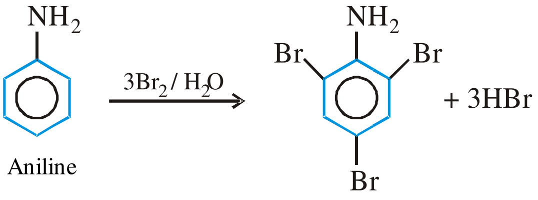
N-Ethylethanamine

N, N-Diethylbenzene sulphonamide (3^0)

In this compound, acidic hydrogen is not joined with N, and so it is insoluble in alkali.

(7) Electrophilic substitution reaction : Aromatic amines give electrophilic substitution reactions. **In case of –NH_2 group electron density is very high on o- and p- position so ortho and para substituted products are obtained.**

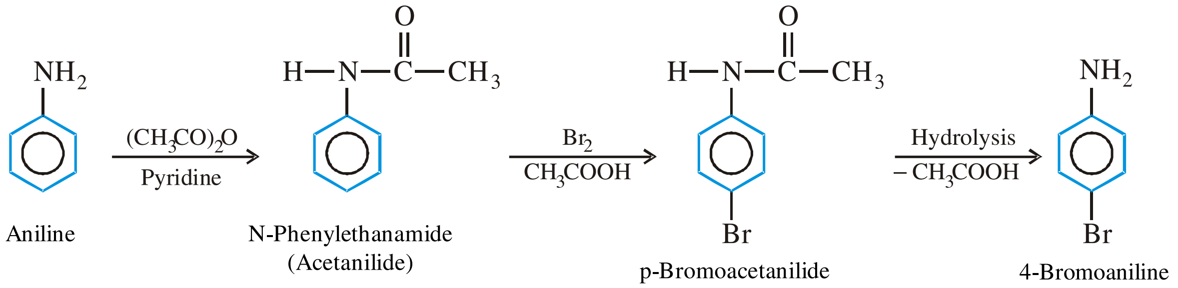
(a) Bromination : At room temperature aniline reacts with bromine water and gives white precipitates of 2,4,6-tribromoaniline.



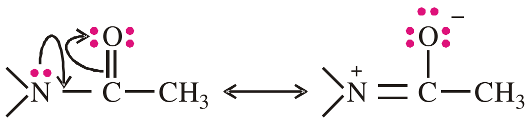
Aniline

2,4,6-Tribromoaniline

If only monosubstituted aniline derivative is desired then first, acetylation of –NH_2 group with acetic anhydride, (electrophilic substitution) is carried out. At the end of this reaction the amide product is hydrolysed so that monosubstituted aromatic amine is obtained.

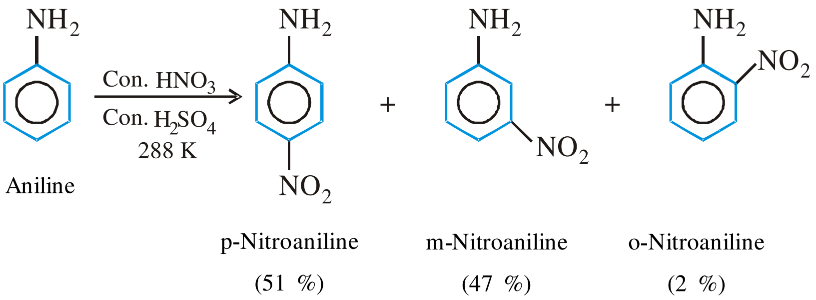


In the above reaction, in the formed acetanilide there is resonance and so the non-bonding electron pair interacts with oxygen atom.

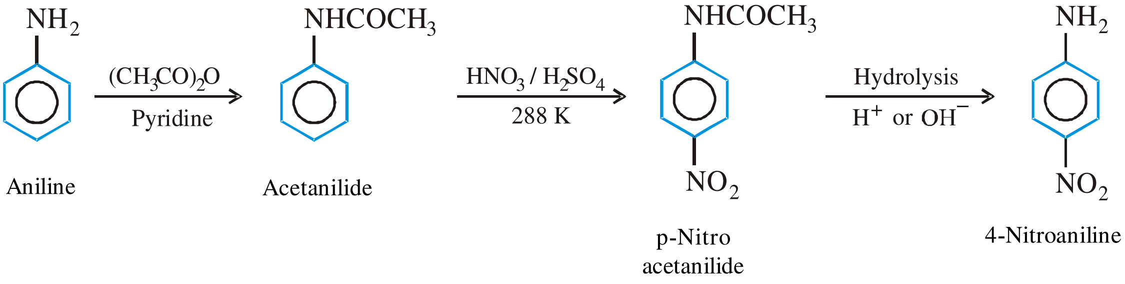


Hence, the electrons are not easily available to benzene for resonance. This functional effect of $–NHCOCH_3$ group decreases compared to $–NH_2$ group.

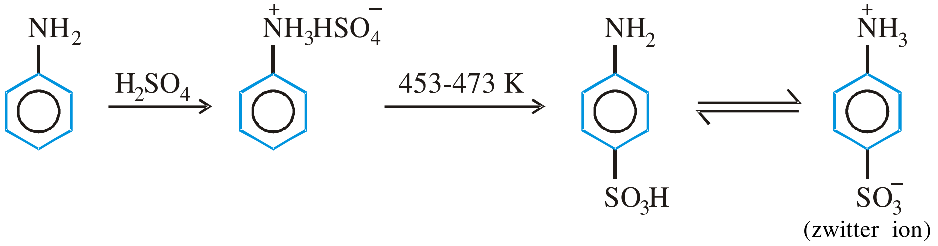
(b) Nitration : Aniline in presence of con. H_2SO_4 reacts with con. HNO_3 at 288 K temperature and mixture of p- and o- nitroaniline with m- nitroaniline are obtained by nitration because the **anilinium ion $-\overset{+}{N}H_3$ formed in acidic medium is m-directing group.**



Here also, to obtain monosubstituted derivative, first acetylation of $–NH_2$ group with acetic anhydride is carried out and then nitration is carried out.



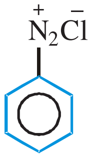
(c) Sulphonation : On reaction of aniline with con. H_2SO_4, anilinium hydrogen sulphate is obtained, which is if heated at 453-473 K temperature product, p-aminobenzene sulphonic acid (sulphanilic acid) is obtained as product.



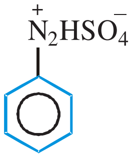
Aniline does not give Friedel-Crafts alkylation and acylation reactions because the catalyst anhydrous $AlCl_3$ used in the reaction is Lewis acid and so it forms salt by combining with aniline. Hence, **nitrogen in aniline attains positive electric charge so it acts as deactivating group for the further reaction.**

6.8 Diazonium Salt

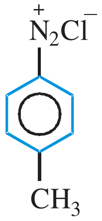
Diazonium salt is shown by general formula as Ar $\overset{+}{N}_2\overset{-}{X}$ **where** $X^- = Cl^-$, Br^-, HSO_4^-, BF_4^- **etc.** $\overset{+}{N}_2\ (-\overset{+}{N}\equiv N)$ **group is called diazonium group.** In their nomenclature diazonium suffix is applied to original hydrocarbon and then the name of negative ion is written. e.g.,



Benzenediazonium chloride

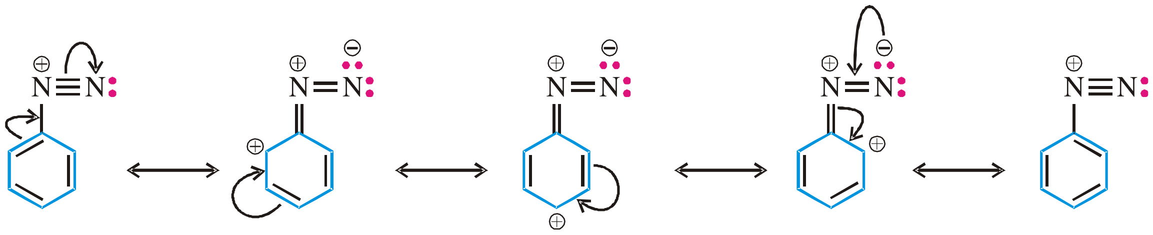


Benzenediazonium hydrogen sulphate



p-Toluenediazonium chloride

Primary aliphatic amine forms highly unstable alkyl diazonium salt while primary aromatic amine which forms arenediazonium salt, is stable due to resonance as shown below.

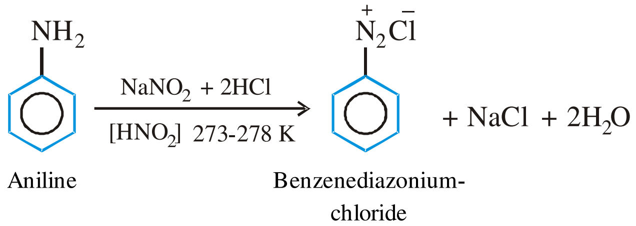


(a) Preparation of benzenediazonium chloride salt : In the reaction between primary aromatic amine and nitrous acid carried out at low temperature, diazonium salt is formed. This reaction is called diazotisation.

A solution of aniline in dilute hydrochloric acid is prepared and, it is cooled to 273-278 K temperature; On adding sodium nitrite, nitrous acid is formed and benzene diazonium chloride (salt) is obtained. As benzenediazonium salt is unstable at higher temperature, it is necessary to keep the temperature 273-278 K.

$$Ar-NH_2 \xrightarrow[\text{[HNO}_2\text{] 273-278 K}]{NaNO_2 + 2HCl} Ar-\overset{+}{N}\equiv N\cdot\overset{-}{Cl} + NaCl + 2H_2O$$

As diazonium salt is unstable, it is used immediately.



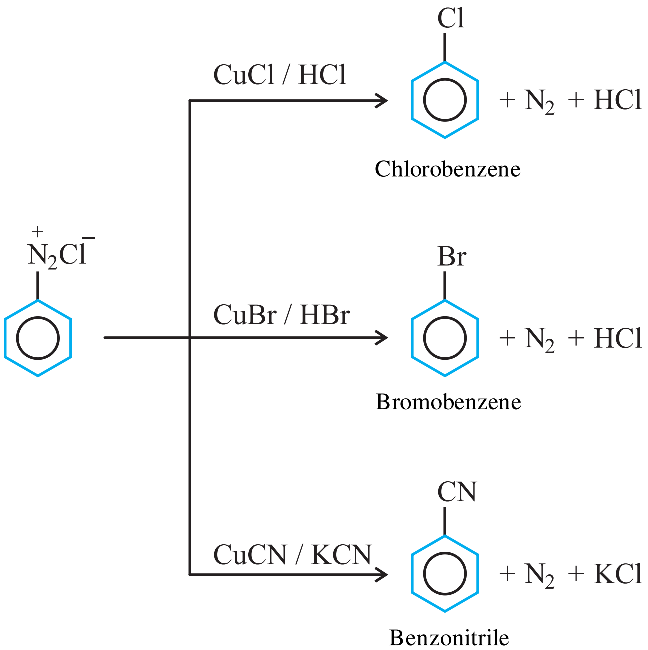
(b) Physical properties : Benzenediazonium chloride is colourless, crystalline solid. It is easily soluble in water and at low temperature becomes stable in solution; but on heating it reacts with water. It easily decomposes in dry state. Benzenediazonium fluoroborate ($C_6H_5N_2^+BF_4^-$) named diazonium salt is insoluble in water and is stable at room temperature.

(c) Chemical reactions :

(A) Displacement of nitrogen : Diazonium group ($-\overset{+}{N} \equiv N$) can be substituted by groups like Cl^-, Br^-, I^-, CN^-, OH^- and dinitrogen (N_2) is removed in the form of gas because of substitution reaction.

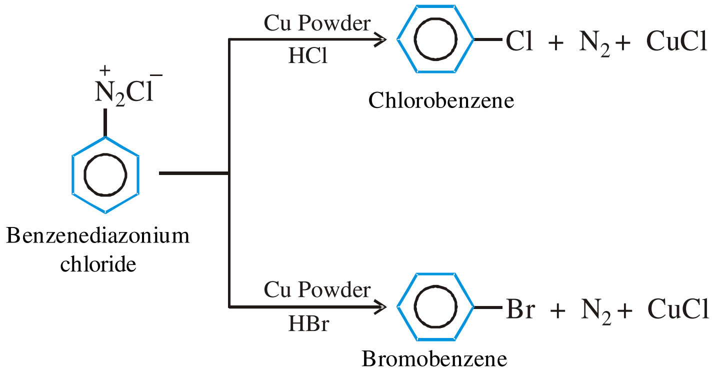
(i) Diazonium salt reacting with cuprous chloride in HCl gives chlorobenzene, with cuprous bromide in HBr gives bromobenzene and with cuprous cyanide in KCN gives benzonitrile (cyanobenzene). These reactions are called **Sandmeyer reactions.**

$$Ar-\overset{+}{N}_2\overset{-}{Cl} \xrightarrow{CuX\,/\,HX\ (X\,=\,Cl^-,\ Br^-,\ CN^-)} Ar-X+N_2+HCl$$



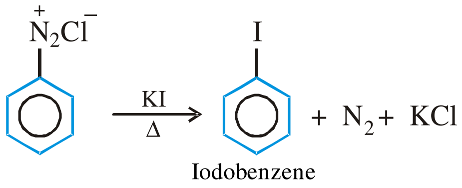
(ii) On reaction of diazonium salt in presence of copper powder with HCl or HBr, chlorobenzene or bromobenzene are respectively obtained. This reaction is called Gatterman reaction.

$$Ar-\overset{+}{N}_2\overset{-}{Cl} \xrightarrow[HX\ (X\,=\,Cl,\ Br)]{Cu\ powder} Ar-X+N_2+CuCl$$



(iii) On heating diazonium salt with potassium iodide, iodobenzene is formed.

$$Ar-\overset{+}{N}_2\overset{-}{Cl}\xrightarrow[\Delta]{KI}Ar-I+N_2+KCl$$

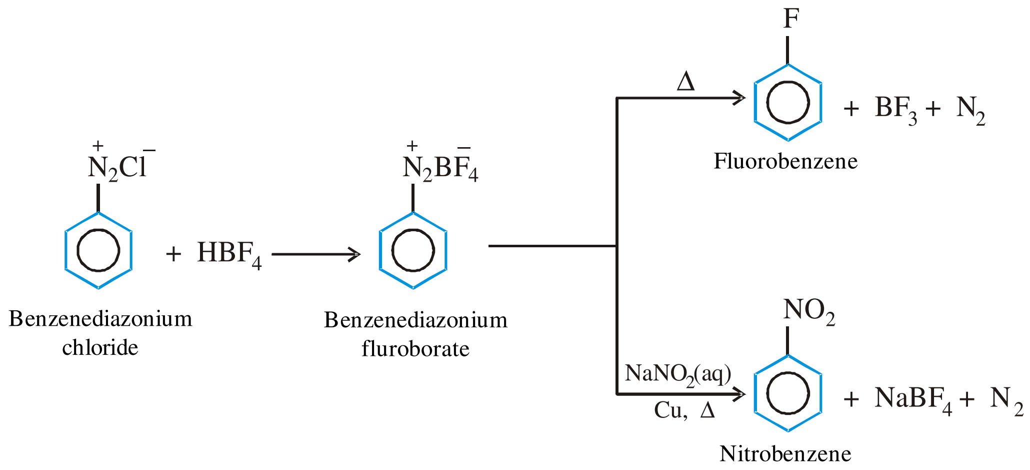


(iv) Precipitates of diazonium fluoroborate are obtained by reaction of diazonium salt with fluoroboric acid (HBF_4). On heating, it decomposes and gives fluorobenzene.

In addition, nitrobenzene is obtained by heating diazonium fluoroborate with aqueous solution of sodium nitrite ($NaNO_2$) in presence of copper metal.

$$Ar\overset{+}{N}_2\overset{-}{Cl}+HBF_4\rightarrow Ar\overset{+}{N}_2BF_4^-\xrightarrow{\Delta}ArF+BF_3+N_2$$

$$Ar\overset{+}{N}_2\overset{-}{Cl}+HBF_4\rightarrow Ar\overset{+}{N}_2BF_4^-\xrightarrow[Cu,\ \Delta]{NaNO_2(aq)}ArNO_2+NaBF_4+N_2$$



(v) Benzene is obtained by reduction of diazonium salt with weak reducing agent like hypophosphorus acid (Phosphinic acid, H_3PO_2) or ethanol.